

COAL PHOTOLUMINESCENCE: MODIFICATION OF SURFACE PROPERTIES AND GEOCHEMICAL AND TECHNOLOGICAL IMPLICATIONS

Alan Davis and Gareth D. Mitchell

Coal & Organic Petrology Laboratories, Department of Geosciences,
105 Academic Projects, Penn State University, University Park, PA 16802

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INTRODUCTION

The luminescence behavior displayed by vitrinite across the coal rank range upon exposure to microscopic blue- and UV-light irradiation, has been explained by Lin et al. (1) using the molecular-phase concept. Two peaks occur in the trend of vitrinite luminescence intensity with rank. The first of these, at the low maturity end of the series represented by peats and lignites, displays the highest intensity levels. This "primary fluorescence," is considered to be due to the presence of lignin-derived structures (2); it is almost eliminated by about the subbituminous C/B boundary owing to the progressive luminescence quenching which accompanies condensation. It is the second peak, centered at high volatile A bituminous rank (reflectance of about 0.9%), which Lin et al. have attributed to the development of the mobile or molecular phase within the vitrinite. The same coals give the highest yields of chloroform solubles. It is these extractable components which are responsible for the luminescence response of the vitrinites; whereas the aromatic and polar fractions of hexane solubles were highly luminescent, the chloroform-extracted residue of mildly pre-heated vitrinite was not visibly luminescent. This residue is considered to represent the aromatic network which is too highly condensed to luminesce in bituminous coals; delocalization of electrons in the macromolecules within this rank range causes intense quenching.

With increasing time of exposure to UV or blue light under an air objective, the luminescence intensity displayed by vitrinite undergoes progressive or variable changes in patterns which are rank dependent. Davis et al. (3) have shown that this phenomenon, termed "alteration", results mainly from photochemical oxidation; it does not occur when an inert medium is used instead of air. A cationic dye, Safranin O, which is sensitive to oxidized coal surfaces, responds positively to the air-irradiated surfaces. FTIR spectroscopy reveals that a major change resulting from the air irradiation is an increase in carbonyl functional groups.

One purpose of this paper is to review some of the geochemical factors, in addition to rank, which influence the luminescence response of vitrinite. Another is to discuss how the molecular-phase concept has been applied to the results of quantitative luminescence photometry of the products of dry, catalytic hydrogenation. However, most of the results reported here are concerned with an investigation of the relationship between oxygen functionality and hydrophobicity. Advantage has been taken of the photo-oxidation technique to modify the surface chemistry of vitrinites so that variation in contact angle and floatability can be related to specific changes in FTIR-determined oxygen functionality.

INFLUENCE OF DEPOSITIONAL ENVIRONMENT UPON VITRINITE LUMINESCENCE

Although rank has a dominant influence in determining the luminescence behavior of coals, there is also some influence exerted by the depositional environment. Several investigators have observed higher luminescence intensities displayed by vitrinites deposited in a marine-influenced environment compared to those not so influenced. Rathbone and Davis (4) reported a positive correlation between luminescence intensity and total sulfur of an iso-rank series of bituminous coals; they discussed the possibility that the phenomenon might be related indirectly to a greater incorporation of bacteria-derived lipids into coals deposited in a marine setting. Zhang et al. (5) have suggested an alternative mechanism through which sulfur-linked aliphatic structural units acquired during early coalification has directly enhanced vitrinite luminescence intensity. Py-gc/ms and solid-state ^{13}C nmr of vitrinites and luminescence measurements on model compounds led to the conclusion that bacterially reduced sulfur species can vulcanize functionized lipids onto the macromolecular phase. In contrast, increased levels of phenolic compounds present in low-sulfur freshwater vitrinites are associated with lower luminescence intensities.

LUMINESCENCE PHOTOMETRY OF LIQUEFACTION RESIDUES

Quantitative luminescence photometry was one technique used to interpret the structural changes involved during dry, catalytic hydrogenation (6,7). Measurements were taken on the unextracted

liquefaction products and on the subsequent extracts. For example, hydrogenation experiments were performed using a high volatile bituminous coal and an impregnated molybdenum catalyst at 400°C for four different reaction times. The absence of a liquid vehicle is essential so that the liquid products are not removed from the coal. With increase in time up to 60 min, the luminescence intensity of the unextracted residues increased progressively and markedly from the zero reading obtained with the fresh coal. This increase closely paralleled the proportion of chloroform extracts obtained from the series of hydrogenated coals, a correspondence suggesting that the luminescence is a response from relatively low molecular weight materials representing both the molecular phase of the coal and products from the breakdown of the network. Indeed, the luminescence of the vitrinite residue, induced by hydrogenation, showed a red shift (increase in wavelength) as hydrogenation temperature was increased from 350 to 400°C; this shift is consistent with the increased generation of asphaltenic materials from the network. The chloroform extract of the 400°C residue was highly luminescent (the residue was not); two physically distinct components were recognizable. The component with by far the highest luminescence intensity had a spectral peak wavelength corresponding to that of the oil (hexane-soluble) fraction of the hydrogenation products, whereas that of the less luminescent component had a spectral peak corresponding to that of the asphaltene fraction.

PHOTO-OXIDATION AND HYDROPHOBICITY OF BITUMINOUS COALS

Severe oxidative weathering has a negative influence on the behavior of coals in most industrial processes including cleaning. As coals are increasingly oxidized they become less hydrophobic and more difficult to separate from mineral matter by flotation.

The surface photo-oxidation of bituminous coals which occurs as a result of blue- and UV-light irradiation shares many similarities with naturally weathered coal. Therefore, light of 390-490 nm has been used to prepare oxidized vitrain surfaces. These have been employed in experiments to establish correlations among surface oxygen functionality, surface hydrophobicity, flotation yield and, as a readily measurable index of oxidation, luminescence intensity.

An optical microscope was used to measure luminescence intensity (in N_2) and alteration (in air), and to photo-oxidize freshly polished surfaces of vitrains collected from a suite of coals of varying bituminous rank (hVcb to mvb) using a blue-light flux. Irradiations were conducted for 0, 1, 5 and 10 mins. The change in near-surface chemical functionality was measured using reflectance-mode FTIR. Contact-angle measurements were made on these same irradiated surfaces to obtain a correlation among chemical changes, luminescence intensity and wettability.

Scribe marks were cut perpendicularly across selected vitrain bands on polished blocks of coal, and successive 200µm diameter areas were irradiated in two adjacent lines parallel to each mark to create 0.4mm wide oxidized zones. During the course of the irradiations, photometric readings were obtained of the change in luminescence intensity with time (alteration).

A sessile drop technique was used to determine the change in surface wettability. Using a syringe and micro-pump, a drop of distilled water was advanced from the fresh vitrain surface across the photo-oxidized area and contact angles measured at regular intervals. These same areas were subsequently relocated for measurement of variation in functional group chemistry using reflectance-mode FTIR.

A comparison of the luminescence, contact angle and FTIR spectra for the fresh and varyingly photo-oxidized vitrain surfaces for three of the coals studied is given in Figures 1 and 2. Luminescence intensity changes characteristically during irradiation in air; for fresh bituminous coals there is either a negative (intensity decrease) or dual (decrease followed by increase) response, depending upon coal rank (first column, Figure 1). The reflectance FTIR spectra (Figure 2) show a progressive increase in absorbance in the carbonyl region (~ 1775 - 1650 cm^{-1}) and a decrease in the aliphatic region (~ 3030 - 2850 cm^{-1}) with irradiation time. The spectra also suggest that the O-H region near 3450 cm^{-1} may increase upon irradiation. Considering these results, the influence of photo-oxidation on surface wettability (second column, Figure 1) is predictable, i.e., the magnitude of change in contact angle increases with irradiation time. These effects decrease with rank.

The results suggest that the luminophores on the surface of fresh bituminous coals are initially quenched by oxygen, causing a decrease in emission intensity, with only marginal influence upon

near-surface chemistry and wettability. However, with increasing exposure, an increase in the spectral region occupied by ketones, aldehydes and esters suggests a variety of reactions involving carboxylic acid groups and anhydrides that would affect the intensity of luminescence alteration.

CONCLUSIONS

Rank is the dominant influence in determining the luminescence behaviors of coals; however, measureable effects representing the depositional environment can also be encountered. In marine-influenced environments, lipoidal material may have become incorporated into the coal precursor molecule through a sulfidization process, leading to an enhancement of luminescence intensity.

The results of quantitative luminescence spectrometry support the conclusion that the more intense levels of coal hydrogenation in a series of dry, catalytic experiments were achieved by disruption of the macromolecular network and the production of asphaltenes.

Blue-light irradiation using photometric microscopy provides a means of progressively oxidizing the surfaces of vitrains. The reflectance FTIR measurement on irradiated areas shows an increase in the carbonyl and decrease in aliphatic regions that are similar to results observed in laboratory and natural oxidation studies. The changes in infrared spectra and wettability are more pronounced with increasing radiation time and with lower rank. Some contribution to the oxidation of coals exposed at the face of strip mines and in stockpiles may have arisen as a result of exposure to the ultraviolet irradiation of sunlight.

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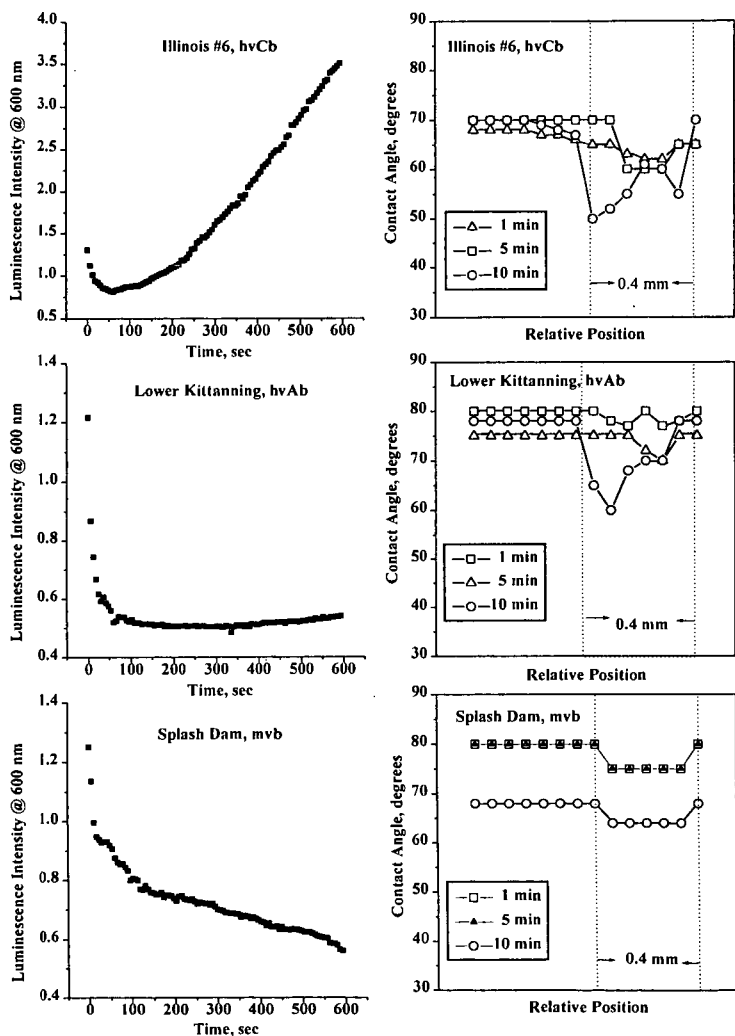


Figure 1. Comparison of luminescence alteration and contact angle measurements on fresh and photooxidized areas of three bituminous coals

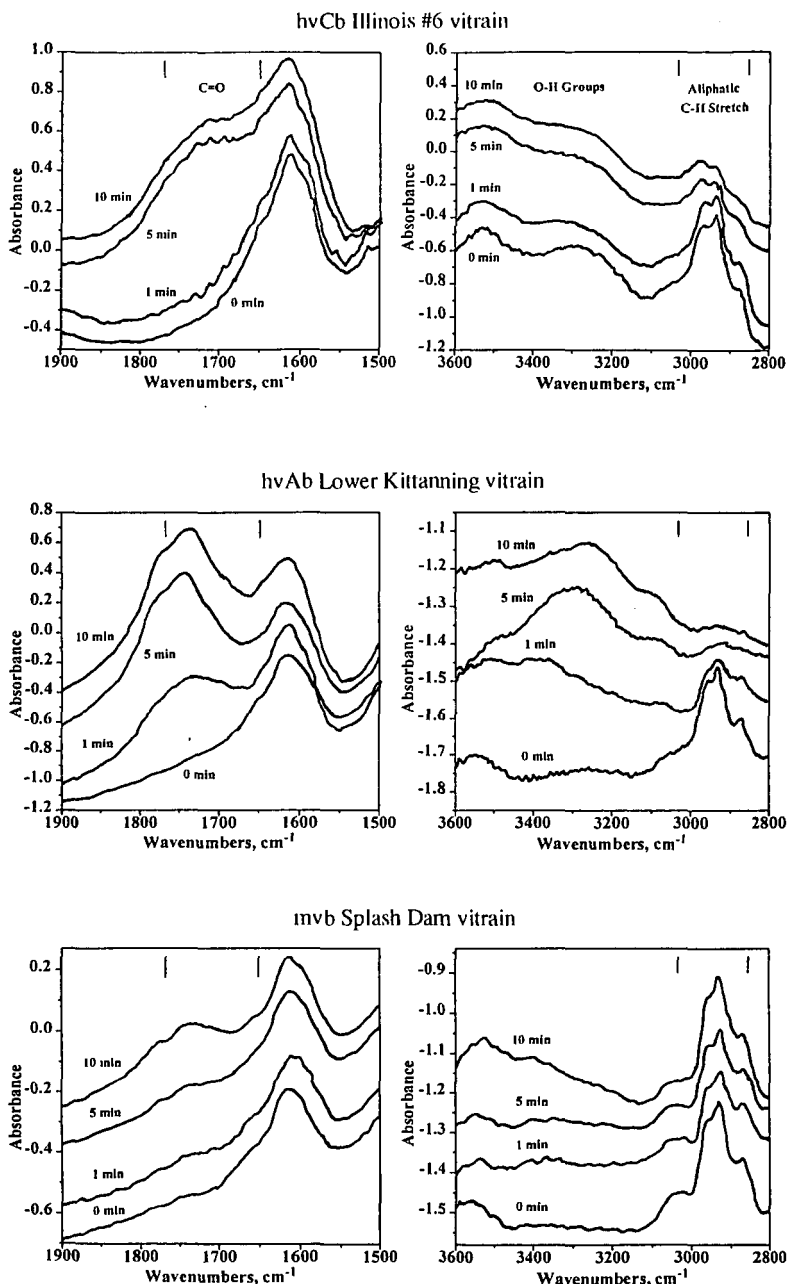


Figure 2. Comparison of FTIR spectral regions for fresh (0 min.) and irradiated surfaces (1, 5 and 10 min.) of three bituminous coals.